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*Publication date:*  
2006

[Link back to DTU Orbit](#)

*Citation (APA):*  
Due-Hansen, J., Rasmussen, S. B., Kustov, A., Siret, B. (Ed.), Tabaries, F. (Ed.), & Fehrmann, R. (2006). *Regeneration of Pt-catalysts deactivated in municipal waste flue gas with H<sub>2</sub>/N<sub>2</sub> and the effect of regeneration step on the SCR catalyst*. Paper presented at 8th European Congress on Catalysis, Turku, Finland.  
<http://www.europacat.org>

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# Regeneration of Pt-catalysts deactivated in municipal waste flue gas with H<sub>2</sub>/N<sub>2</sub> and the effect of regeneration step on the SCR catalyst

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## Introduction

Burning municipal waste or sludges instead of landfill depositing is an important issue from an environmental point of view, since this “waste to energy” conversion also implies several benefits such as control of toxic emissions and heavy metal waste, etc. In this connection, the treatment of gaseous emissions containing carbon and nitrogen oxides as well as volatile organic compounds has been of increasing concern in recent years. However, deactivation of noble metal supported catalysts for CO oxidation is an important industrial problem and have been widely studied in recent years.

This work focuses on a case with severe deactivation of a commercial Pt/TiO<sub>2</sub> catalyst for CO oxidation during ageing in a sewage sludge waste incineration plant operating at 250°C. It was observed that the catalyst deactivated few days after startup of the gas cleaning system. Lab-scale tests revealed that siloxanes were the most severe poison although acidic sulfur compounds also caused deactivation. A method for catalyst regeneration was developed i.e. addition of H<sub>2</sub>/N<sub>2</sub> gas to the off-gas was observed to restore the catalysts activity [1].

Addition of reductive hydrogen containing gas to the off-gas also affects the catalytic redox mechanism of the Selective Catalytic Reduction (SCR) unit, used for removal of nitrogen oxides, which is installed after the CO oxidation catalyst. Part of this study therefore also concentrates on the impact of H<sub>2</sub>/N<sub>2</sub> gas on the V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst.

## Experimental

Samples of the fresh and deactivated commercial proprietary Pt/TiO<sub>2</sub> based catalysts were obtained from the incineration plant. Model Pt/TiO<sub>2</sub> catalysts were prepared by dissolving 131.6 mg H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (38% Pt, Fluka) in 100 ml water with 10 g TiO<sub>2</sub> (anatase, Millennium Chemicals, pre-calcined at 500°C), similar to the procedure described by Benvenutti et al. [2]. The mixture was stirred overnight. Water was removed in vacuum at 60°C. After drying, residual (HCl) was removed by calcination at 400°C for about 30 h, ending up with a 0.5 wt% Pt/TiO<sub>2</sub> model catalyst. Samples of this model Pt/TiO<sub>2</sub> catalyst were poisoned by several compounds, of which hexamethyldisiloxane (HMDS, >98.5%, Fluka) was found to be the most severe. The catalyst was poisoned with HMDS to obtain bulk molar ratio between HMDS and platinum of 2:1.

## Results and discussion

Upon poisoning the fresh model catalyst with HMDS, a significant decrease in CO oxidation activity was observed, and the temperature of 50% conversion of CO to CO<sub>2</sub> was shifted from 213°C to 250°C (Reaction conditions: 10% O<sub>2</sub>, 0.2% CO, balance N<sub>2</sub>, GHSV = 30,000 h<sup>-1</sup>). The influence of HMDS on Pt/TiO<sub>2</sub> was also studied with FTIR, the results are depicted in Fig. 1 (left). It was found that the poisoning is reversible, and after treatment in 10% H<sub>2</sub>/N<sub>2</sub>

gas (Formier) for 80 min, which is followed by the complete disappearing of Si-CH<sub>3</sub> groups signal in the FTIR spectra (Fig. 1, right).

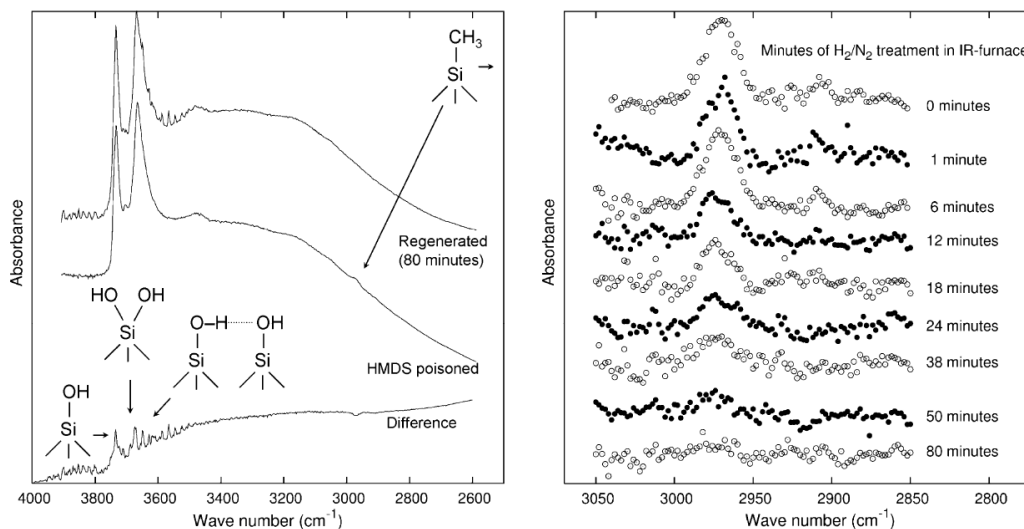


Figure 1. High temperature-FTIR (250°C) spectra of HMDS poisoned Pt/TiO<sub>2</sub> catalyst. Left: Poisoned catalyst before and after treatment with 10% H<sub>2</sub>/N<sub>2</sub>. The difference spectrum shows the conversion of HMDS-derivates into silanols. Right: Blow-up of background corrected Si-CH<sub>3</sub> band disappearing over time due to the treatment with 10% H<sub>2</sub>/N<sub>2</sub> mixture.

In this work we also present our latest results regarding the effect of hydrogen on the operating SCR catalyst. Preliminary studies are being performed on the effect of H<sub>2</sub>/N<sub>2</sub>- and H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub>-mixtures on the SCR catalyst in terms of NO-SCR activity. The treatment with hydrogen in a 2% H<sub>2</sub>, 8% O<sub>2</sub> gas mixture show little effect on the performance of the SCR unit, although the vanadium is reduced to V<sup>3+</sup> by the hydrogen, but quickly returns to the distribution of V<sup>4+</sup> and V<sup>5+</sup> under operating conditions after few minutes in the NO SCR gas as observed by in-situ EPR spectroscopy.

## Conclusions

The deactivation of Pt-catalysts for CO oxidation has been studied in relation to use in sewage sludge municipal waste burners, where HMDS was found to poison the industrial catalyst in a similar way to the model Pt/TiO<sub>2</sub> catalyst. A promising regeneration procedure was developed based on reduction with hydrogen. This procedure seems so far to have negligible effect on the performance of the SCR catalyst.

## Acknowledgements

LAB SA, France is thanked for financial support of this investigation.

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